METHOD TO PREVENT RECESSION LOSS OF SILICA AND SILICON-CONTAINING MATERIALS IN COMBUSTION GAS ENVIRONMENTS

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BACKGROUND OF THE INVENTION

The invention relates to silicon-containing materials in combustion gas environments, and more particularly, relates to a method to reduce or prevent the material loss of silica and silicon-containing materials in high temperature combustion gas environments, such as encountered in industrial land-base turbines, aircraft engines, automobiles and heat exchangers.

Silicon-based monolithic ceramics, such as silicon carbide, silicon nitride, and silicon-containing composites, including continuous-fiber reinforced ceramic composites, are attractive candidates for high temperature structural applications, such as component parts for gas turbines, aircraft engines, and heat exchangers. These silicon-containing materials are particularly appealing because of their excellent high temperature properties and lower density. For instance, in combustion gas environments, a performance benefit is obtained by replacing cooled metal components with uncooled or reduced cooling silicon-containing ceramic components. Material substitution of hot gas path components with such ceramics yields higher output power, improved thermal efficiency and reduced NOx emissions. Depending on the size of the component part and the mechanical specifications that the component must meet in service, silicon-containing composite ceramics including continuous or discontinuous-fiber reinforced ceramic composites, such as silicon carbide fiber reinforced silicon carbide or silicon-silicon carbide matrix composites, are sometimes selected over monolithic ceramics because of superior thermal and mechanical shock resistance, higher damage tolerance and strain-to-failure. Examples of discontinuous fiber reinforced composites include composites reinforced with silicon carbide whiskers. Examples of monolithic ceramics are silicon carbide, silicon nitride, and silicon-silicon carbide ceramics.

A primary advantage then of silicon-containing ceramics or silicon-containing composites (herein, silicon-containing ceramics or composites) over metals is their superior high temperature durability which enable higher turbine rotor inlet temperatures. In addition, they exhibit low coefficient of thermal expansion and lower density in comparison to nickel-base superalloys. The relatively high thermal conductivity of silicon-containing composite systems is similar to nickel-based alloys at the use temperatures.

The gas turbine component parts where silicon-containing ceramics or silicon-containing composites are being considered include the shroud and the combustion liner. The shroud forms the turbine outer flowpath and creates a sealing surface over the rotor buckets. It is a primary element in the turbine tip clearance and roundness system and is segmented in larger machines. It serves as a heat shield and insulates the turbine casing from the hot gas stream temperature. As part of the flow path, the shroud must have sufficient oxidation/corrosion resistance and be structurally sufficient to meet design life requirements for the engine temperature, pressure and flow environment.

The combustion liner contains the combustion reaction zone and conveys the hot gases to the turbine inlet. In low emissions combustors the flame temperature is minimized to limit production of thermal NOx. This is accomplished by putting most of the compressor air, except for turbine cooling air, through the premixers and minimizing the amount of cooling or dilution air through the liner. Complex thermal gradients and elevated temperatures in liners can lead to excessive distortion in metals causing loss of sealing, restrictions in cooling air flow, and increases in hot side heat transfer. Silicon-containing composites offer low cycle creep-fatigue resistance and very little deformation. As the case with the shroud, the combustion liner must have sufficient oxidation/corrosion resistance. Additional pieces of turbine components comprise nozzles, vanes, blades, buckets and transition pieces.

High oxidation resistance is imparted by formation of a protective silica (SiO_2) film on the silicon-containing ceramic or composite surface. The above proposed applications for the silicon-containing materials position them in direct contact with combustion gases, which are the product of the combustion of liquid fuels or natural gas hydrogen or coal. For natural gas, liquid or coal fuels, the products of combustion contain up to about nineteen percent water vapor by volume dependent on the fuel-to-air ratio. Even higher water vapor levels are obtained for mixtures of natural gas and hydrogen or for pure hydrogen. In an environment containing water vapor and oxygen, thermodynamic calculations indicate the primary reactions which occur for the oxidation of silicon (present for example, as silicon carbide) are:

$$SiC+3/2O_2(g)=SiO_2+CO(g) \tag{1}$$

$$SiC+3H_2O(g)=SiO_2+3H_2(g)+CO(g) \tag{2}$$

Hydrogen and carbon monoxide react together to form water vapor and carbon dioxide. The silica film formed on the silicon-containing ceramic or composite in an oxygen/water vapor gas mixture may simultaneously volatilize by forming a silicon hydroxide or silicon oxyhydroxide species. For instance, some possible volatilization reactions are:

$$SiO_2+H_2O(g)=SiO(OH)_2(g) \tag{3}$$

$$SiO_2+H_2O(g)=Si(OH)_4(g) \tag{4}$$

$$2SiO_2+3H_2O(g)=Si_2O(OH)_6(g) \tag{5}$$

The volatilization of silica results in material loss resulting in reduction of the thickness of the silicon-containing ceramic or composite materials. The observed rates of loss are of the order of a few mils to tens of mils per thousand hours of operation in the combustion gas environment. Depending on the fuel used, such fuel as natural gas, the reaction is favored by high water vapor content (up to about 19% by volume), high pressures (generally up to 30–40 ATM) and high temperatures (up to about 1200–1500° C.) found in many turbine, engine and heat exchanger applications. Thus, for long-term chemical durability of silicon-containing ceramics or composites in combustion environments the volatility of the silica film needs to be controlled during the lifetime of the component.

SUMMARY OF THE INVENTION

The above-identified needs are satisfied by this invention which provides a method to reduce material loss of the silicon-containing ceramics and silicon-containing ceramic